

Copper-Based Metal Flakes, in Particular Comprising Aluminum, and Method for Production Thereof

5 Metallic effect pigments are pigments that exhibit specular reflection on flat, oriented particles (DIN 55944). The interest in lustrous gold-colored effect pigments is great, particularly in the fields of application of printing, lacquer, paint coating, plastic coloring, cosmetics and glass coloring, since the gold-like products have a high aesthetic quality and impart to such coated, imprinted or colored materials
10 an expensive look. Early on it was begun to replace the expensive genuine gold flakes in the decorative field with more cost-effective alternatives.

The best known genuine-gold flake substitute pigments are the so-called gold bronze powders, which consist predominantly of copper/zinc alloys and, depending on their composition, may have different shades of color ranging from red
15 gold to rich gold (Pigment Handbook, Vol. 1, Second Edition, p. 805 ff, Wiley). Gold bronze pigments are produced through atomization of a molten copper/zinc alloy and subsequent grinding of the granules produced by the atomization. During the grinding process, the alloy particles are deformed flake-like and comminuted.
20 In practice gold bronze pigment is predominantly ground dry. To prevent cold welding, a lubricant, such as stearic acid, is added to the utilized granules. A post-treatment of the ground product by brushing or gentle milling in special ball mills serves to improve the luster of the metal pigment and is referred to as polishing. Irregularities in the surfaces of the metal flakes have a luster-reducing

effect. Since the generation of irregularities in the structure of the surfaces of the flakes and different flake thicknesses cannot be avoided during the grinding process, the gold bronze pigments that are produced in this manner do not exhibit the luster that is calculated from the reflectivity of the alloys. Additionally, virtually
5 all gold bronze pigments that are produced via grinding processes display leafing properties, i.e., they float in the medium, which can be attributed to the lubricants added during the grinding process. The manufacture of non-leafing gold bronze pigments requires expensive freeing from lubricant.

10 Attempts to replace genuine gold flakes via iron-oxide-coated mica pigments (G. Pfaff and R. Maisch, Farbe+Lack, Vol. 2, 1955, p. 89-93) or iron-oxide-coated aluminum pigments (W. Ostertag, N. Mronga and P. Hauser, Farbe+Lack, Vol. 12, 1987, p. 973-976) do not achieve their objective regarding the required brilliance. While it is possible to produce interesting shades of color ranging from
15 red gold to green gold via interference effects, it has been shown that the high luster-determining reflection values of metals cannot be achieved via oxidic planes of reflection.

From US 4,321,087 it is known that metals are deposited onto a carrier sheet and
20 pigments are obtained after stripping and comminuting.

As a method for producing metallized layers the customary vapor deposition methods (electron beam technology, resistance radiation heated processes) may be

be used, which are described in detail, for example in G. Kienel (editor)

"Vakuumbeschichtung Vol. 1-5", VDI-Verlag 1995.

In the case of alloys consisting of two or more components, a fractionating occurs
5 due to different vapor pressures. Different evaporation methods (flash evaporation, simultaneous method, or jumping beam method) exist whereby homogeneous alloy layers of any desired composition are producible (G. Kienel).

It is the object of the invention to develop a lustrous gold-colored, highly brilliant
10 metallic effect pigment that does not have the shortcomings of the above-described real-gold substitute products.

It is a particular object to make available a lustrous gold-colored metallic effect pigment with plane-parallel surfaces and low uniform particle thickness, so that
15 the pigment can be applied in all areas of the graphics industry, particularly also in offset printing.

It is an additional object of the present invention to make available a lustrous gold-colored metallic effect pigment in various shades of color ranging from red
20 gold to green gold.

It is an additional object of the present invention to make the lustrous gold-colored metallic effect pigment available in corrosion-stable form, so that no im-

pairment in the luster and shade of the products occurs in the customary fields of application.

It should additionally be producible at economically supportable costs.

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These objects are met with a one-layered flake-like metal pigment with plane-parallel planes of reflection that is composed of a copper-based alloy deposited by condensation from the vapor phase. Preferred suitable alloy partners are aluminum, but also the metals silver, palladium and silicon, either individually or in
10 combination. The coloristics of the novel lustrous gold-colored pigments are determined predominantly by the ratio of copper to the achromatic alloy components. The higher the percentage of copper, the more red gold the flakes are. Silicon increases the color depth of the flakes. Typical compositions of flakes with red gold to yellow gold or green gold luster contain, in addition to copper, 1 to
15 49% aluminum and optionally 0.1 - 6% silicon. The flake thickness is 10 - 100 nm, preferably 20 - 60 nm and can be varied without difficulty. Very thin flakes are partially transparent.

One particular characteristic of the lustrous gold-colored pigments are their perfect plane-parallel surfaces, their undisturbed structural composition and their
20 uniform flake thickness, which permits the highest possible reflection values.

The most important steps of the manufacturing process are the application of a release coat onto a carrier, condensations of the alloy as a film onto the release

coat, stripping of the metallic film, comminuting of the film, and optionally sizing of the pigment particles. The vaporizing of the metals in vacuo takes place according to known methods using the ready-made alloys or the individual metals.

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The inventive pigments exhibit the highest degree of brilliance and are sufficiently corrosion-stable in many fields of application. If a special corrosion stability is required it is possible to improve the stability of the highly lustrous pigments through surface coating. The surface coatings are generally sufficiently
10 thin and have virtually no impact on the luster behavior of the metal flakes. Surface coatings to improve the corrosion behavior may be applied in the vacuum chamber in the course of the metal film deposition, for example through vacuum deposition of SiO_x on both sides of the metal film, or via wet-chemical methods during or after comminuting of the film. Depending on the requirement, protective
15 coatings of SiO_2 , Al_2O_3 , phosphate, phosphoric ester, phosphinic acid, silanes, or combinations of these compounds have proven effective.

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The lustrous gold-colored metal flakes are used for lacquers, paints, dyes, printer's inks, plastic coloring, cosmetics, glass and ceramics.

The following is an explanation in detail:

The present invention relates to a novel effect pigment composed of an alloy. An alloy, in this context, is understood to mean the solid solution of two or more

metals. Surprisingly it is possible to deposit coloristically suitable alloys from the vapor phase in vacuo. Pigments that consist of alloys and are produced by simultaneous condensation of metal vapors have not been known until now.

- 5 Suitable alloys for the development of brilliant genuine-gold substitute pigments via PVD processes are copper-based and contain, for example, as additional alloy components, aluminum and/or silver, palladium and silicon. Among these listed metals, aluminum is the preferred alloy partner of copper, not only because of its superior reflectivity and low specific weight. Silver and palladium percentages in
10 the deposited alloy increase the corrosion stability of the lustrous gold-colored metal flakes, silicon influences the coloristics. The metals may be evaporated individually or as previously molten alloys.

- Coloristically, a wide range between red gold, pale gold and green gold can be
15 created via the composition of the deposited alloy. The color-imparting copper plays the main role in this context. The surfaces of pigments with 90 wt. % copper, for example, have a red gold luster, whereas those with only 60 wt. % copper appear pale yellow. Silicon has a brightness-reducing effect and becomes apparent visually in a greater color depth of the lustrous gold-colored flakes.

- 20 Coloristically interesting compositions lie, for example, at 90 - 99% copper, 10 - 1% aluminum. If very thin flakes are present, they may display partial transparency. Interference effects may have minor impacts on the above-described coloristics.

The thickness of the lustrous gold-colored metal flakes can be adjusted and controlled without difficulty via the evaporation rate of the metals and via the belt speed. For economic reasons, the belt speeds are generally selected between 2 and 5 m/sec. Metal film thicknesses between 10 and 100 nm may be selected in the process, as desired. For the manufacture of lustrous gold-colored metal flakes, thicknesses between 20 and 60 nm are of particular interest. The particle size is adjusted after stripping the metal films from the carrier sheet through mechanical comminuting of the film fragments. The comminuting may take place with suitable agitators, pumps, or with the aid of ultrasound units of the film fragments that are suspended in a solvent. Generally, particle sizes between 3 and 150 μm , preferably between 5 and 50 μm are of interest. As with all effect pigments, the optical appearance may be varied by means of sizing, i.e., setting narrow particle size distributions with different mean diameters. The sizing may be performed, for example, in a decanter.

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The characteristic properties of the gold-colored metal flakes are their high reflectability and a very high tinctorial power of the pigment in the application. The high reflectability is based on the mirror-smooth undisturbed surfaces and the uniform thickness of the flakes. Potential scatter centers are reduced to a minimum. The high tinctorial power of the pigment is based on the low thickness of the individual particles so that a sufficient degree of coverage can be attained already with a comparably small amount of pigment.

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The inventive pigments are produced in such a way that a carrier sheet, for example a PET film or a continuous metal belt is optionally coated with a release coat. The coating of the carrier sheet with a soluble resin or wax may be performed via a dipping or imprinting method.

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The appropriate metals are then evaporated individually or as pre-molten alloy for example in one or more evaporators under high vacuum and condensed onto the carrier sheet.

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The metal film is subsequently stripped and comminuted to pigment particle size in a solvent suitable for the application, such as isopropanol, isopropylacetate, ethylacetate or glycol ether by means of a suitable agitator or a pump that exerts high shearing forces. Ultrasound comminuting may be used in addition or alternatively. Optionally, the pigment particles are also sized.

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To protect the metal surfaces of the inventive pigments from corrosion, it is possible to provide them in an additional step with anticorrosive layers. Since these layers are thin and low refracting, they have virtually no influence on the optical behavior of the pigments. In principle, two methods of applying anticorrosive

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layers are possible: on one hand by vapor deposition of a double-sided protective layer during the evaporation process, on the other hand by precipitation of a passivating layer during or after comminuting of the film fragments. The vapor deposition of protective layers during the evaporating process is performed in the sequence protective layer, alloy film, protective layer, for which low-soluble but

easily evaporated materials are generally selected, such as SiO_x or MgF_2 . The precipitation of a passivation layer is performed as a wet-chemical reaction. The precipitation of a thin SiO_2 layer, expediently via a sol-gel process through hydrolysis of silanes and subsequent silanol treatment has proven suitable, also the

5. precipitation of aluminum oxide, silicon oxide, phosphate, phosphoric acid, phosphoric esters, phosphinic acid, silanes, organically modified silicates, titanates, zirconates or methacrylate-based polymer layers or combinations of these compounds.

10 The invention will be explained in more detail below based on preferred embodiments.

Example 1

15 In a roll coater by firm Leybold Heraeus, a PET carrier film of $48\ \mu\text{m}$ thickness, which is coated with a release coat, is coated with a copper/aluminum alloy under high vacuum. The release coat consists of acetone-soluble methylmethacrylate resin and is printed on in advance in a separate processing step. The vacuum is adjusted to $5 \cdot 10^{-4}$ mbar.

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The speed with which the carrier film is unwound is 4 m/s. The copper/aluminum alloy with a copper content of 92% is evaporated in a boat via resistance heating at a rate that results in a metal film thickness on the moving carrier sheet of 40 nm. After completion of the coating the roll coater is flooded with nitrogen, the

metallized PET roll is removed and treated with acetone in a stripping station.

Through dissolving of the release coat the metal film is separated from the carrier film. The metallic film fragments are concentrated in a centrifuge and separated from the release-coat containing acetone solution. The filter cake is then entered
5 into an isopropanol solution, where the film is comminuted over the course of 20 minutes. The suspension in which the metal flakes are present is a 12% suspension.

The obtained pigment suspension exhibits lustrous gold-colored pigment particles
10 of the highest brilliance. The mean particle size of the flakes is 10 μm (Cilas). Chemical analyses show that the pigment contains 92% copper and 8% aluminum. X-ray analyses reveal that the elements are present in homogenous alloy form.

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Example 2

a) In the set-up described in example 1, a copper-aluminum-silicon film is deposited. This is performed analogous to example 1, with the difference that, in addition
20 to the evaporation source for copper/aluminum, an additional one is installed for silicon. The copper/aluminum alloy that is made available for the evaporation contains 94% copper. The thickness of the film that is precipitated from the vapor phase is set to 45 nm. Stripping of the film and comminuting of the film fragments to pigment size takes place as in example 1.

The pigment that is obtained in suspension has a deep red golden luster. It contains 2% silicon. The mean particle size, according to Cilas measurements, is 11 μm .

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b) Stabilization:

1000 g of the above produced 12% pigment suspension in isopropanol are heated to the boiling point and 11 g tetraethoxysilane and 10 g water are added. A 10% aqueous solution DMEA is subsequently added using a Dosimat until a pH of 8 is reached. The mixture is stirred for 2 hours while maintaining the pH. 1.4 g di-phenyl dimethoxysilane, which is dissolved in 12 g isopropanol, is then evenly dosed in over the course of 4 hours while stirring. Subsequently, 0.5 g 3-aminopropyl-trimethoxysilane (Dynasilan AMMO) are added and the mixture is cooled over the course of 10 hours while stirring.

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The metal pigment is then present in a corrosion-stabilized form.